THE CLEAVAGE OF QUATERNARY AMMONIUM SALTS OF ALKYLTHIOSULFURIC ACIDS

BY
RICHARD GEORGE HANDRICK
B. Chem., Cornell University, 1937
M.S., University of Illinois, 1939

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

It has been shown[1,2] that both the alkali salts and quaternary ammonium salts of benzylthiosulfuric acid are unstable in the presence of aqueous alkali. The action of dilute sodium hydroxide and even of sodium carbonate upon sodium S-benzylthiosulfate produces benzyl disulfide and the salts of benzoic acid, thiobenzoic acid, α-toluenesulfinic acid, and sulfurous acid. The known products[2] of the reaction of benzyldimethylphenylammonium S-benzylthiosulfate with 10 per cent sodium hydroxide are dimethylaniline, benzyl sulfide, benzyl disulfide, and sodium sulfite.

In order to determine whether the decomposition products are derived from the anion or cation, substituted quaternary ammonium salts of substituted benzylthiosulfuric acids were allowed to react with dilute aqueous potassium hydroxide.

Discussion of Results

Following the methods described in a previous work[2] benzyldimethylphenylammonium S - *p* - bromobenzylthiosulfate was prepared and allowed to react with a hot 10 per cent solution of potassium hydroxide. The compounds recovered as products of this reaction were dimethylaniline, *p*-bromobenzaldehyde, *p*-bromobenzoic acid, a red oil, a white organic salt containing potassium, and a basic, viscous brown oil.

After long standing at room temperature *p*-bromobenzyl disulfide crystallized from the red oil. The residual oil was oxidized by hydrogen peroxide to benzyl *p*-bromobenzyl sulfoxide and benzyl *p*-bromobenzyl sulfone, indicating benzyl *p*-bromobenzyl sulfide was originally present in the red oil.

The organic potassium salt was readily oxidized by dilute potassium permanganate to a new salt containing potassium and by hot nitric acid to *p*-bromobenzoic acid. The original

potassium salt was converted to a magnesium, a silver, and a *p*-bromobenzylisothiouronium salt. It reacted with methyl iodide to produce a new potassium salt in which a benzyl group had been replaced by a methyl group, as shown by analysis and by isolation of benzyl iodide from the reaction mixture. This new potassium salt, or the corresponding silver salt, reacted further with methyl iodide to produce another compound in which a methyl group had replaced the metallic atom.

When the free acid obtained from the original potassium salt was heated at 150°, it decomposed to form *p*-bromobenzaldehyde, *p*-bromobenzaldehyde benzyl mercaptal, and sulfur dioxide.

These reactions indicate the presence of a sulfinate ($-SO_2^-$) group, a *p*-bromobenzal ($BrC_6H_4CH=$) group, and a benzylthio ($C_6H_5CH_2S$) group. Consideration of the analytical data and of the fragments described shows that the original potassium salt is potassium α-(α'-toluenethio)-*p*-bromo-α-toluenesulfinate. The product of reaction with excess methyl iodide may be either the sulfone formed by replacement of the potassium atom and the benzylthio group by methyl groups, or the inner salt (sulfonium sulfinate) formed by S-methylation of α-methanethio-*p*-bromo-α-toluenesulfinic acid. The physical properties of the substance indicate the latter structure.

Numerous attempts were made to synthesize the original potassium salt and its methylation products. No desired product was isolated nor could any satisfactory conclusions be drawn from the results obtained.

The synthesis and alkaline decomposition of *p*-bromobenzyldimethylphenylammonium S-benzylthiosulfate, of benzyldimethylphenylammonium S-*p*-nitrobenzylthiosulfate, and of *p*-nitrobenzyldimethylphenylammonium S-benzylthiosulfate were carried out. The products obtained were similar to those from the decomposition already described. However, no organic potassium salt corresponding to that described above was obtained.

When benzyldimethylphenylammonium S-*p*-bromobenzylthiosulfate was allowed to react with potassium hydroxide in

the presence of an equimolar quantity of benzyldimethylphenylammonium chloride, a water-soluble substance containing no nitrogen, halogen, or metal was isolated and no potassium α-(α'-toluenethio)-*p*-bromo-α-toluenesulfinate was found. Although analysis agrees with the formula $C_{24}H_{27}O_5S$, no attempt was made to clarify the structure.

The variety of products from these decomposition reactions indicates that more than one type of reaction occurs. An ionic mechanism may explain the formation of the unsymmetrical sulfide; a free radical mechanism may explain the formation of the disulfide.

Bibliography

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VITA

The writer was born on January 1, 1917 at Johnson City, New York where he attended the primary and high schools. Having been graduated valedictorian of his class in June 1933, he entered Cornell University the following September. He was graduated in 1937 with the degree of Bachelor of Chemistry. For nearly a year following his graduation he worked as control chemist with Agfa Ansco, Binghamton, New York. In September 1938 he was admitted to the Graduate School of the University of Illinois from which he received the degree of Master of Science in June 1939. He served as Assistant in Chemistry, 1939-41, and as a Fellow in Chemistry, 1941-42.

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